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A STUDY OF THE EXTRACTIVE ACTION
OF BENZENE AND XYLENE ON COAL
AT HIGH PRESSURES

BY

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THESIS

FOR THE

DEGREE OF BACHELOR OF SCIENCE

IN

CHEMISTRY

COLLEGE OF LIBERAL ARTS AND SCIENCES

UNIVERSITY OF ILLINOIS

1922

1922
F53

UNIVERSITY OF ILLINOIS

May 31, 1922

THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

Richard Stoner Fisher

ENTITLED *A study of the Extractive Action
of Benzene and Xylole at high Pressures*

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF *Bachelor of Science*

in Chemistry

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The writer wishes to acknowledge the ready advice and helpful criticism of Dr. T. E. Layng in the work of which this is the report.

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A STUDY OF
THE EXTRACTIVE ACTION OF BENZENE AND XYLENE
ON COAL AT HIGH PRESSURES.

INTRODUCTION.

The primary purpose of a study of the products obtained by the action of solvents on coal is to formulate a workable theory of coal carbonization. Of all industrial operations which are carried out on such an immense scale, the manufacture of coke is perhaps the least understood. In spite of the great advance the industry has made in substituting the by-product recovery oven for the older bee-hive type, the carbonization of coal is still very largely a rule of thumb process.

Why, then, a theory of carbonization? Good coke is made by the present methods. One - half of the world's supply of coal is in the United States. What need is there of knowing the details of how coke is formed as long as plenty of good coke can be made without that knowledge? The best answer to this query is the fact that at the present rate of consumption, the available supply of coal fit for coking will be exhausted in the next fifty years. Since coal is such a very bulky substance, it is cheaper to ship iron ore to the country which produces the coal than to import the coal necessary for metallurgical processes. Thus no country which does not have an adequate supply of coal from which good metallurgical coke can be made can hope to be a great producer of iron and steel goods no matter what the quantity and the quality of its iron ore.

It is imperative, then, if we wish to retain our present position as a great steel manufacturing nation, that some method be found to coke these coals which are at present regarded as non - coking. Obviously the best way to go about finding why anthracites and some of the lower grades of coal will not coke is to find how and why the so called "coking" coals do form coke. To that end we must direct our attention to a study of the development of a theory of carbonization.

THE CARBONIZATION OF COAL.

Coal carbonization aims at the production of coke. According to V. B. Lewes (2)*, coke is "the name given to the solid residue left by the destructive distillation of coal and many other carbonaceous substances, and contains as its chief constituent carbon, together with the mineral matter or ash of the original body, such portions of the residues as the temperature employed has failed to drive out of the mass, and occluded gases".

HISTORICAL

The carbonization of coal to form coke grew out of the necessity of finding a substitute for charcoal. Charcoal had been, up to this time, the main fuel used in extracting iron from its ores, but the supply of wood available for the production of charcoal was rapidly being exhausted. The first attempts to coke coal were quite naturally patterned after the methods then in general use in charcoal burning. Coal was heaped on the ground, ignited, and plastered with wet coal dust to blanket combustion.

*N. B. Numbers in parenthesis refer to bibliography.

Later a small chimney was introduced in the center of the coal mass to allow free escape of the gases. The pile of coal was ignited by introducing burning coal through this chimney and combustion was checked as before. This method of coke manufacture was, of course, very wasteful. Not only the gas evolved but even a part of the coal itself was consumed in heating the mass. The old bee - hive coke oven grew out of this early practice. These ovens, built in groups of heavy masonry, had the effect of retaining the heat better than the old "meiler" heaps. But the ovens were still heated by the destruction of all the gaseous products of distillation and a part of the coal itself. Gradually we have come to a realization of the immense value of the by - products of coal distillation, and to the conviction that we have too long been wasting our natural resources. The by - product coke oven has come into wide use as a direct result of this feeling, together with the greater economy of operation. These ovens are fired externally and the valuable products are recovered before the gas is burned to heat the ovens.

At the same time has come a somewhat similar development of the other of the carbonization industries - gas manufacture. The growth of this industry has been marked by a dogged singleness of purpose which has at times overlooked the best interests of the industry as a whole. Gas production managers have been intent upon obtaining the largest possible volume of gas from a ton of coal. In doing this they have frequently been guilty of forgetting quality in their search for quantity. They have also, up to this time, steadily refused to devote any thought to a possible improvement of the coke produced as a by - product of the industry. Coke in the gas industry has always been considered more of a necessary

evil that a possible source of profit. The result has been an inferior quality of coke - porous, friable, and hard to dispose of. It is to be hoped that the gas manufacturer will soon take a more lively interest in fuel conservation and, by using a somewhat lower temperature and paying a little more attention to the coke produced, give us a better quality of gas and ^{an} ample quantity of coke which, if not adaptable to metallurgical uses, may be used extensively for domestic purposes. Such a coke - cheap, and easily ignited would be a boon to our smoke infested cities.

IMPORTANCE OF THEORY OF CARBONIZATION.

What, then, is the problem involved in the theory of carbonization? Good coke is being made every day. What more do we want? The problem is simply this. Only certain, rather definitely restricted classes of coal will coke. Why is this? What makes coal coke? What is lacking in anthracites that they will not coke? Why will lignites not coke? Can these non - coking coals be made to coke? These are some of the questions facing the carbonization industries today. Why do we want to coke these coals? We have coal enough to supply us with metallurgical coke for many years. Why not burn the rest raw? Because when raw coal is burned in the ordinary type of domestic furnace from 60 - 80 % is wasted. Worse, for this waste is also responsible for the great smoke nuisance in the cities and so impairs the cheerfulness and even the health of the inhabitants. If coke were used exclusively for domestic and office heating, great wealth in the form of dye - stuffs, medicinal basis, germicides, fertilizers, and light oils for use as a substitute for gasoline, would be saved every year.

METHODS OF ATTACKING THE PROBLEM.

Three methods have been used in attacking the problem of obtaining a satisfactory theory for the carbonization of coal. These are:-

1. Microscopic examination.
2. Low temperature carbonization.
3. The action of solvents on coal.

Reinhardt Thiessen (3), has done some very exact work on the microscopic examination of coal. However, since this phase of the work has more bearing on the identification and examination of the individual constituents of coal than on any definite theory of carbonization, we will at present consider the last two means of attack. A very interesting theory of the formation of coal has been built up around this work of Thiessen by David White. (3) We will consider White's theory a little later in connection with a preliminary study of the constitution and formation of coal.

Before starting on a review of the work that has been done in the fields of low temperature carbonization and solvent action it will be well to present some of the ideas and accepted facts concerning the substance and origin of coal. What is coal? Where did it come from? Almost any school boy will embark glibly enough on an explanation of the latter question, but ask him what coal is and he has no answer. Or he may say that coal is carbon and class it with diamond and graphite as a form of that element. As a matter of fact there is probably no free carbon in coal. And when it comes to an attempt to enumerate the substances present in coal we may as well admit that we do not know. We only know that coal contains compounds of carbon, hydrogen, oxygen, nitrogen, and sulphur arranged in innumerable chemical combinations and mixed

with inert mineral matter in varying proportions. This complicated structure of coal together with the fact that coals from the same neighborhood may be widely different in character, is very largely responsible for the altogether different results which may be obtained by two independent investigators working on similar problems. In 1878, Green defined coal as "a compact stratified mass of mumified plants subjected to arrested decay in various stages of completeness and free from all except a very low percentage of foreign material".

White (3) claims that all coal was laid down in beds analogous to our peat beds of today. All kinds of vegetation from the largest club mosses to the smallest fungi went into the deposits. Hence the wide divergence in the characters of different coals. The climatic conditions existing at the time were very largely responsible for the formation and burial of these peat beds. The warm atmosphere led to a quick luxuriant growth which, because of the coarse structure due to such rapid growth, was easily attacked by decay. According to White, one foot of surface peat was laid down in ten years. Because of dehydration and densification caused by the increased pressure and temperature, it would take about one hundred years to get a one foot stratum of peat twenty feet below the surface of the ground. Three feet of this compressed peat would be required to produce a one foot stratum of coal. The change from the original vegetable matter to coal is divided into two parts. First, the dead vegetable matter is subjected to biochemical reactions to give peat. Then the peat is buried and subjected to dynamochemical processes to form coal. Plant materials are composed chiefly of celluloses and proteins. The cellulosic part makes up the large bulk to form a framework. The pro-

teins are concerned in the vital functions of the plant. These compounds differ widely in their resistance to various agencies. The proteins are relatively unstable while the celluloses are attacked with more difficulty.

At the death of the plant, governed by conditions in the bog, a partial decomposition, elimination, and chemical reduction sets in. This biochemical change is brought about chiefly by organic agencies - fungi at first and bacteria later. The most volatile parts of the plant constituents are removed first, the next follow, etc., until the most resistant parts are left in a residue called peat. This process of decomposition and reduction, begun in the peat chiefly by biochemical means, is taken up and continued by dynamochemical agencies into and through successive stages of decomposition into the various grades of coal. So much for the composition and formation of coal. We will now turn our attention to the most common methods of studying coal carbonization.

THE FRACTIONAL CARBONIZATION OF COAL.

The classic example of carbonization work is that done in England by Burgess and Wheeler (4). Similar work has been more recently attempted in this country by Porter and Taylor (5). The results and conclusions drawn by Porter and Taylor differ widely from those of Burgess and Wheeler. This does not mean at all that the results of one or the other were in error, for the experiments were both carried out with great care, but it does show the effect of a different grade of coal studied under slightly different conditions by different men. The personal equation plays an important part in such studies of coal.

Studying the gaseous products obtained from 200 grams of powdered South Yorks, Silkstone bituminous coal at temperatures of 100', 200', 300', 350', 400', and 450'C, Burgess and Wheeler reached the following conclusions:

Coal contains two types of compounds of different degrees of ease of decomposition; the one, the least stable, yielding the paraffin hydrocarbons and no hydrogen; the other, decomposing with greater difficulty and yielding hydrogen alone or hydrogen and the oxides of carbon. Probably the difference between one coal and another is determined mainly by the proportions in which these two types of compounds exist, anthracite, for example, containing but little of the more unstable constituent. The presence of carbon monoxide is more probably due to the liberation of water from hydroxy compounds and the subsequent reaction of the steam thus formed with carbon. In a later paper Wheeler states that he believes that the hydrogen yielding constituent is what he calls the "cellulosic" and the paraffin yielding the "resinic" part of the coal. The experimental work of Burgess and Wheeler has been confirmed by similar work carried out by Vignon on some French coals. Vignon's discovery of a critical temperature between 700' and 800'C., at which there is a marked increase in the evolution of hydrogen.

The conclusions drawn by Burgess and Wheeler have, however, been severely criticised by Porter and Taylor(5). These investigators object to the statement that after all the less stable paraffin yielding "resinic" constituent has been decomposed, the decomposition of the more stable hydrogen yielding "cellulosic" part sets in about 700'C. Wheeler's statement that water of decomposition begins to be evolved about 200'C., shows

that a partial decomposition of the "cellulosic" constituent has begun at that early point. Porter and Taylor found that:

1. More than two - thirds of the organic substance of coal is decomposed below 500°C., but there is a variation among different kinds of coal in their ease of decomposition.

2. The first decomposition occurring in any type of coal as the temperature is raised is the breaking down of certain oxygen - bearing substances related to cellulose, from which chiefly water of decomposition, CO_2 , and CO . are produced.

3. Other decompositions, producing paraffins both liquid and gaseous, begin at an early stage. Whether or not such decompositions become the predominating type below 500°C. depends on the character of the coal, and, as a general rule, the higher the oxygen in the coal, the less will be the proportion of hydrocarbons and tar in the volatile matter.

4. Secondary decompositions of the primary volatile products occur quickly and easily at temperatures of 730°C., and above.

The theoretical conclusions which Porter and Taylor have drawn from these results are as follows:

"All kinds of coal consist of cellulosic degradation products more or less altered by the processes of aging, together with derivatives of resinous substances, vegetable waxes, etc., in different proportions more or less altered. They all undergo decomposition by a moderate degree of heat, some, however, decomposing more rapidly than others at the lower temperatures. The less altered cellulosic derivatives decompose more easily than the more altered derivatives and also more easily than the resinous derivatives. The cellulosic derivatives decompose so as to

yield water, carbon monoxide, carbon dioxide, and hydrocarbons, giving less of the first three products the more matured and altered they are. The resinous derivatives, on the other hand, decompose on moderate heating so as to yield principally the paraffin hydrocarbons, with probably hydrogen as a direct decomposition product. The more mature bituminous coals, having good coking properties, contain a large percentage of resinous derivatives, and their cellulosic constituents have been highly altered. The younger bituminous or sub-bituminous coals are constituted of cellulosic derivatives much less altered than those in the older coals. They undergo a large amount of decomposition below their fusion point and possibly for that reason many of them do not coke.

THE ACTION OF SOLVENTS ON COAL.

The study of solvent action should be divided into two parts:

1. The action of reagents which separates out some of the constituents of coal in an altered form. Under this head come sulphuric and nitric acids, potassium and sodium hydroxides, pyridine, aniline, quinoline, phenol, bromine, and oxygen.

2. True solvent action which is believed to extract from the coal substance some of the unchanged coal constituents. Some of the substances which are supposed to exert only a solvent action on coal are benzene, chloroform, alcohol, ether, petroleum, ether, acetone, toluene, xylene, and di-phenyl ether.

The action of reagents we must pass over without much discussion. No results obtained from a study of bodies extracted from coal by such reagents can carry much weight because the existence of such bodies as such in coal cannot be definitely proved.

For instance, it has been found that the substance obtained from coal by extraction with pyridine usually contains almost twice the amount of nitrogen as was originally present in the coal. This shows that the pyridine base has entered into combination with some of the acidic substances of the coal making any further study of the products obtained useless.

In regard to solvent action, Bone (1) says:

"The difficulty is to find solvents that will differentiate sufficiently between the main constituents of the coal and extract a large proportion of some one of them, without at the same time having some depolymerising or other similar action upon the whole structure". Most of the solvents which, without much question, do extract the coal constituents unchanged do so in such minute quantities as to make the task of obtaining sufficient amounts of the substances for experimental purposes almost hopeless. J. A. Smythe (1) found that ethyl ether and petroleum ether had very little effect on the coal while benzene, chloroform, and alcohol extracted quantities varying between 1.8 and 3.0 percent of the coal. Similar experiments have been more recently carried out by many workers with practically the same results.

Interesting possibilities are disclosed in some recent work by Fischer and Gluud (1) in Berlin on the action of benzene on coals at pressures of some 50 atmospheres. By using a temperature of 270°C., and a pressure of 55 atmospheres, 6.7 % of extract was obtained from a coal which had previously yielded only 0.1 % on extraction with boiling benzene. No study of the products obtained was made aside from the determination of their physical properties. No proof was offered that, at the temper-

atures employed, decomposition did occur except that no gas was noticed on opening the cooled bomb. In one of the experiments, hydrogen sulphide gas was noticed on opening the bomb. This was taken as an indication that some decomposition had occurred. This work of Fischer and Gluud, however, undoubtedly opens up great possibilities of finding a means of obtaining sufficient quantities of such extracts from coal for farther experimental work.

EXISTING STATUS OF THE THEORY OF CARBONIZATION.

The existing theories of coal carbonization have been very well crystallized in the following statement of Lewes' opinion:

"Many theories have been put forward as to the nature of the binding material in coke. Some declare that it is the residuum of the semi - fused constituents in coal, whilst Wedding and others consider that it is carbon deposited by the decomposition of heavy hydrocarbon vapors, which is undoubtedly the cause of the carbon hairs found in coking. It seems most probable, however, that the cementing material is due to liquid products, the most volatile of which are driven off as vapors, leaving pitch, which carbonizes and binds the mass into coke".

A somewhat different theory has been recently advanced by Dr. T. E. Layng* of the University of Illinois.

For the formation of good coke three conditions must be fulfilled.

1. There must be a bond forming material present.

2. The material to be bonded must have delivered all of the adsorbed oxygen and oxides of carbon before the decompo-

*This theory was presented in class room discussion.

sition of the bond forming material.

3. The bond forming material must not distil without decomposition.

As may be readily seen, this theory conforms well to a number of well known facts about the coking of coal. Anthracites will not coke because they lack the bond forming material. The better grades of bituminous coals conform to all three conditions and therefore give good coke. The lower grades of bituminous coals and lignites are easily oxidizable. Oxygen is adsorbed and the oxides of carbon are formed. These gases are liberated at the time of the decomposition of the bond forming material and prevent good contact of the bonding material with the material to be bonded.

THE PURPOSE OF THIS INVESTIGATION.

The purpose of this investigation is two - fold:

First, to find, if possible some method of extracting the coking constituent from coal in satisfactory quantities and with as little change as possible.

Second, to investigate, with the aid of the substances obtained from the coal, the above theories of carbonization.

EXPERIMENTAL.

Extraction of Coal with Benzene under Pressure.

Various forms of bombs were tried in the beginning of this work. The first type used was a small model of the steel bomb used by Fischer and Gluud. A seven inch length of four inch steel pipe was threaded at both ends and fitted with caps. A mixture of litharge and glycerine was used as a cementing agent and later lead was melted into the caps in an attempt to make the bomb leak - proof, but the pressure desired could not be maintained. In the second attempt several ten inch lengths of one inch pipe welded at one end and fitted with a cap at the other were used. This type was also discarded because the capacity was too small and leaks still developed. The most satisfactory results obtained were with the use of an empty mercury container. 100 grams of coal powdered to pass a sixty mesh sieve and about two liters of benzene were charged into the bomb and the plug screwed in tightly and sealed with a smoothly mixed paste of litharge and glycerine. This bomb was found to be almost entirely leak - proof at the pressures used. The analysis of the coal used which was from Franklin County, Illinois, is given in Table 1, of the section devoted to data. The bomb was placed in an electric furnace and kept at a temperature of from 210' to 240'C. for 24 - 48 hours. (see table 2). At the end of this time the bomb was opened and the solvent was decanted off rapidly through a suction filter leaving as much of the coal as possible in the bomb. Any coal on the filter was returned to the bomb and fresh solvent was added as before. The benzene solution of the third

of these extractions was practically colorless showing that all of the material extractable with benzene was removed in the first two extractions. The benzene solution of the extract was strongly fluorescent. This solution was again filtered to remove the last traces of suspended coal and evaporated to dryness in a current of nitrogen. The residual coal after the last extraction was washed on the filter with alcohol, then with ether and dried in a current of nitrogen. The procedure in the case of the extractions with xylene was exactly the same excepting that seven extractions were necessary to completely exhaust the coal of extractable material. The results (see table 3), show that in the case of the xylene extractions approximately one - fourth of the coal substance was dissolved out of the coal under conditions of temperature and pressure which preclude any possibility of decomposition of either the coal or the solvent.

The comparison between the ultimate analysis of the coal, extract, and residue shows a close agreement in the values obtained for the analysis of the coal by actual experiment and by calculation from the corresponding values of the extract and residue. The value obtained for sulphur is too low. This may be ascribed to a loss of some of the more volatile organic sulphur compounds due to exposure to the temperature necessary to drive off the last traces of the xylene from the extract. The values for oxygen and hydrogen reflect the high heat value caused by some of the solvent not removed from the residue and possibly from the extract. The analysis of the residue was corrected for an ash value which was too high, due to extraneous material from the bomb and the litharge glycerine mixture used to seal it.

The carbonization data (see Tables 5 and 6) is of interest both as a support of Dr. Layng's theory of carbonization and as farther evidence in the controversy between Burgess and Wheeler on the one hand, and Porter and Taylor on the other. The main constituents of the gases obtained from a carbonization of the residue up to 350°C. are oxygen and carbon dioxide. Between 350° and 450°C., the residue, which corresponds to what Wheeler calls the "cellulosic" part of coal, yields mainly hydrogen, oxygen, and the oxides of carbon together with quite a large percentage of hydrocarbons of the marsh gas series. In the carbonization of the residue, the evolution of hydrogen sulphide was first noticed at 420°C. No tar was noticed in the distillation of the residue.

The fraction of gases collected from the extract up to 350°C., contained mainly hydrocarbons of the marsh gas series with appreciable quantities of hydrogen, carbon monoxide and oxygen. The fraction from 350° - 450°C., consisted mainly of hydrogen with some hydrocarbons. Hydrogen sulphide evolution began at 240°C. A large quantity of tar of specific gravity less than one was collected.

Various coking tests were made and are tabulated after Table 6 in the data.

CONCLUSIONS.

1. In the opinion of the writer, the most important result obtained in this investigation was the discovery of a new method of extracting the coking constituent of coal in quantities large enough for experimental purposes. The coking tests made were all upon one gram samples and as such are possibly not entirely indicative of the results which may be obtained on larger samples. The writer believes that work along the line herein explained will go on in these laboratories and that extractions will probably be made on several kilos of coal at a time in autoclaves using xylene as a solvent. In this way enough of the coking constituent could be obtained in the course of several weeks to permit more exhaustive investigations.

2. The results obtained from the fractional carbonization of the extract and residue seem to indicate that both sides are right in the controversy between Burgess and Wheeler, and Porter and Taylor. The main constituents of the gas obtained from the residue up to 350°C., are oxygen and the oxides of carbon. The largest single constituent of the gas from the residue between 350 and 450°C., is hydrogen, in accordance with the claims of Burgess and Wheeler. The extract, in the lower fraction, yields mainly the paraffin hydrocarbons as is agreed by both factions, but in the fraction from 350' - 450'C., the main constituent is again hydrogen which agrees with the results of Porter and Taylor, but is contradictory to those of Burgess and Wheeler.

The sharp distribution of organic and pyritic sulphur between the extract and the residue is shown by the fact that the evolution of hydrogen sulphide from the extract begins at 240'C.,

while in the case of the residue it is not apparent until 420°C., is reached.

The coking tests which were made tend to substantiate the theory of carbonization which has already been attributed to Dr. Layng of this University. The residue from the xylene extraction showed no coking tendency whatever. This shows the effect produced when the bond forming material is removed. When the extract and residue were mixed in the correct proportions, a good hard coke was obtained. Oxidized residue mixed with the correct amount of extract gave a very soft sooty coke. After carbonization some of this oxidized residue was again mixed with extract and yielded a good, hard coke. This test shows the effect of oxygen on the residue where it is unprotected by the extractable portion. Oxygen is adsorbed and combines with the coal substance. Oxygen and the oxides of carbon are liberated at the temperature of decomposition of the bond forming material and tend to prevent the formation of a suitable bond.

DATA

Table 1.

The Proximate and Ultimate Analysis of the Coal Used.

Coal from Franklin County, Illinois.

	As received	Moisture and ash free.
Moisture	9.48	-
Ash	9.45	-
Volatile matter	38.58	47.63
Fixed carbon	42.49	52.37
B. T. U.	11,701.	14,446.
Carbon	63.70	78.64
Hydrogen	4.96	6.02
Oxygen	9.42	11.64
Nitrogen	.97	1.21
Sulpher	2.02	2.49

Table 2.

Extraction Data.

	Extraction with Benzene	Extraction with Xylene.
Temperatures used	210 - 240°C.	210 - 240°C.
Pressure	250-375#/sq.in.	180-200#/sq.in.
Weight of coal used	100gm.	100gm.
Number of charges of solvent for each extraction	2*	7
Volume of solvent used in each charge	2 liters	2 liters
Extraction time for each charge	24-48 hrs.	24-48 hrs.

(* A third charge of benzene was introduced into the bomb
in an attempt to make a more complete extraction but after
extraction the solvent was only slightly discolored.)

Table 3.

Comparative Yield of Extracts obtained
from Benzene and Xylene.

Percentage original coal obtained
as extract.

	Benzene	Xylene.		
	As r'c'd.	M. & A. free	As r'c'd	M & A free
First Extraction	4.8	6.0		
Second Extraction	5.3	6.6		
Third Extraction			22.91	28.2
Fourth Extraction			24.85	30.7

Table 4.
A Comparison of the Ultimate analysis of Coal,
Extract, and Residue.

	Xylene extract	Residue As r'c'd	Corrected ash basis	Coal calculated from extract and residue	Coal by analysis
C	85.96	54.42	57.28	63.90	63.70
H	7.13	-	5.99	6.20	4.96
O	5.42	-	13.29	11.43	9.42
N	.42	.98	1.04	.89	.97
S	.95	1.50	1.58	1.44	2.02
Moist.	.07	6.96	7.33	-	9.48
Ash	.15	17.53	13.50	-	9.45
B. T. U.	16,499.	10,667.	11,229.	12,387.	11,701.

Fractional Carbonization of Extract.

Five gram sample of xylene extract.

Sulpher begins to decompose at 240°C.

Heavy yield of light tar from 200 - 220°C.

Table 5.

Analysis of Gaseous Products of the Carbonization of Extract.

	Gases up to 350°C.		350 - 450°C.	
	Nitrogen free	Vol. in c. c. from 100 gm. ext.	Nitrogen free	Vol. in cc from 100gm.
CO ₂	4.9	94	4.1	177
O ₂	12.6	237	2.6	110
Unsat.	4.7	86	.7	31
Aromatics	.8	14	.4	18
H ₂	20.3	282	53.3	2275
CO	10.8	202	4.7	201
CH ₄	19.6	367	23.6	1007
C ₂ H ₆	26.3	497	10.5	433

Fractional Carbonization of Residue.

Sulphur begins to decompose at 420°C.

Table 6.

Analysis of Gaseous Products of Carbonization of the Residue.

	Gases up to 350°C.		350 - 450°C.	
	Nitrogen free %	Vol. in c.c. from 100 gm. of extract.	Nitrogen free %	Vol. in c.c. from 100 gm. of extract.
CO ₂	60.7	646	16.1	540
O ₂	30.8	277	15.5	518
Unsat.	.5	4	2.8	92
Aromatics.	.0	0	.5	14
H ₂	1.8	17	38.4	1285
CO	3.7	34	5.9	199
CH ₄	.9	8	13.3	447
C ₂ H ₆	1.6	13	7.5	249

Coking Tests.

A. With benzene extract and residue.

Extraction with benzene did not visibly impair the coking qualities of the residue.

Benzene extract melts from 115 - 130°C.

B. With xylene extract and residue.

Residue from xylene extraction shows no coking tendency.

100 % extract softens quickly and swells to a very great extent. Much of a one gram sample will be lost by this swelling. A light, porous, fluffy coke remains.

15 % extract 85 % residue gives a rather poor, soft coke.

30 % extract 70 % residue gives a hard, black, porous coke.

Compares favorably with coke of original coal except that some of the silvery luster is lacking.

A portion of the residue was set aside and exposed to the action of the air and moderate heat. After several weeks of this atmospheric oxidation a coke test was made with 70 % of this oxidized residue and 30 % extract. The mixture showed only a very slight caking tendency. The coke obtained was very soft and sooty. Some of this oxidized residue was then heated in a covered crucible to coking temperature and a portion mixed with extracts as before. Again a coke sample of good quality and texture was obtained.

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